Supplementary Material

Ir-catalyzed C-H Activation in the Synthesis of borylated Ferrocenes and Half Sandwich Compounds

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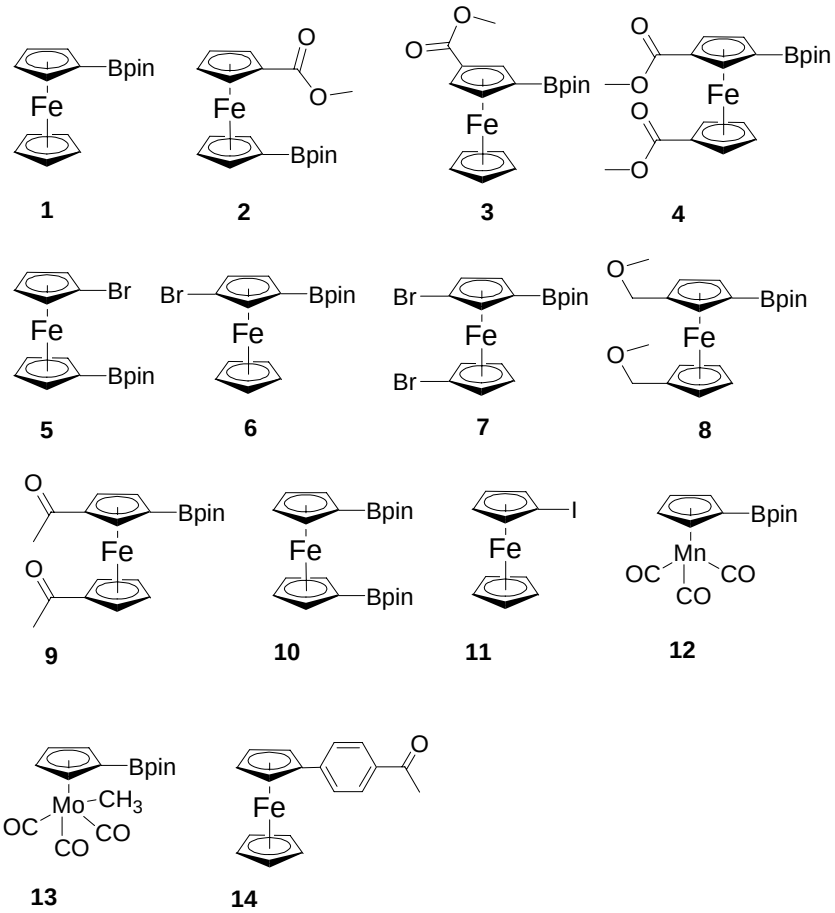
General. All reactions and experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Column chromatography was performed using Silica MN60 (63-200 μm). For gas chromatography, Perkin-Elmer Autosystem with a Varian CP-SIL-8 column was used. NMR spectra were recorded at 293 K with a Bruker Avance 500 and Bruker AC 300. ^{1}H NMR spectra were referenced to residual protonated impurities in the solvent (C_6D_6 = 7.15 ppm) and ^{13}C NMR to the solvent signal (C_6D_6 = 128.4). The coupling products obtained were characterized by ^{1}H and ^{13}C NMR spectroscopy. Ferrocene, cymantrene, bis(pinacolato)diboron, pinacolborane, 4,4′-di-*tert*-butyl-2,2′- bipyridine were purchased from Aldrich. $[Ir(OMe)(cod)]_2$[1], bromoferrocene,[3] 1,1′- dibromoferrocene,[3] 1,1′-dimethylferrocene, (methoxycarbonyl) ferrocene, 1,1′-(methoxycarbonyl) ferrocene, 1,1′-di(methoxymethyl)ferrocene[5] were prepared according to literature procedures.
The purity of the compounds was verified by GC. The carbon atoms bonded to the boron atoms were not observed due to line broadening.



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9 **10** **11** **12**
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The following ferrocenes were prepared according to the general procedure:

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, FcBpin.
^{1}H NMR δ 1.12 (s, 12H), 3.83 (s, 5H), 4.19 (t, 2H, *J* = 1.8 Hz), 4.65 (t, 2H, *J* = 1.8 Hz); ^{13}C NMR δ 25.0, 68.8, 72.3, 74.4, 83.0.

1-(Methoxycarbonyl)-1'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, 1,1'- Fc(COOCH$_3$)(Bpin).
^{1}H NMR δ 1.12 (s, 12H), 4.16 (t, 2H, *J* = 1.9 Hz), 4.25 (t, 2H, *J* = 1.8 Hz), 4.59 (t, 2H, *J* = 1.8 Hz), 4.92 (t, 2H, *J* = 1.77 Hz); ^{13}C NMR δ 25.5, 51.5, 71.3, 72.1, 74.2, 76.3, 76.5, 83.7, 171.3.

1-(Methoxycarbonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, 1,3- Fc(COOCH$_3$)(Bpin).
^{1}H NMR δ 1.12 (s, 12H), 3.33 (s, 3H), 4.10 (s, 5H), 4.7 (dd, 1H, *J* = 1.3 and 1.2 Hz), 5.02 (dd, 1H, *J* = 1.3 and 1.2 Hz), 5.46 (t, 1H, *J* = 1.2 Hz); ^{13}C NMR δ 25.5, 51.5, 70.8, 74.5, 76.4, 77.30, 77.37, 83.7, 171.2.

1,1'-Di(methoxycarbonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, 1,1',3-Fc(COOCH$_3$)$_2$(Bpin).
^{1}H NMR δ 1.12 (d, 12H, *J* = 3.6 Hz), 3.55 (s, 3H), 3.59 (s, 3H), 4.14 (m, 2H), 4.62 (dd, 1H, *J* = 1.3 and 1.2 Hz), 4.87(m, 1H), 4.92 (m, 1H), 5.03 (dd, 1H, *J* = 1.4 and 1.2 Hz), 5.42 (t, 1H, *J* = 1.3 Hz). ^{13}C NMR δ 23.6, 23.5, 49.9, 50.0, 71.0, 71.2, 71.7, 72.9, 74.0, 76.2, 76.8, 76.9, 82.3, 168.2, 168.3.

1-Bromo-1'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, **1,1'-Fc(Br)(Bpin)**.
^{1}H NMR δ 1.12 (s, 12H), 3.87 (t, 2H, *J* = 1.9 Hz), 4.22 (t, 2H, *J* = 1.8 Hz), 4.44 (t, 2H, *J* = 1.3 Hz), 4.61 (t, 2H, *J* = 1.7 Hz); ^{13}C NMR δ 24.6, 68.2, 69.9, 73.3, 74.5, 75.1, 83.0.

1-Bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, **1,3-Fc(Br)(Bpin)**.
^{1}H NMR δ 1.12 (s,12H), 4.15 (s, 5H), 4.21 (t, 1H, *J* = 1.9 Hz), 4.31 (t, 1H, *J* = 1.7 Hz), 4.87 (t, 1H, *J* = 1.9 Hz). ^{13}C NMR δ 24. 9, 67.8, 69.5, 76.2, 76.9, 79.1, 83.3.

1,1'-Di(bromo)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, **1,1',3- Fc(Br)$_2$(Bpin)**.
^{1}H NMR δ 1.12 (s, 12H), 3.82 (m, 1H), 3.91 (m, 1H), 4.87 (m, 1H), 4.23 (dd, 1H, *J* = 1.2 and 1.2 Hz), 4.27 (dd, 1H, *J* = 1.2 and 1.2 Hz), 4.36 (m, 2H), 4.78 (t, 1H, *J* = 1.1 Hz). ^{13}C NMR δ 25.0, 68.8, 70.6, 71.2, 73.3, 73.7, 76.0, 77.1, 78.5, 83.5.

1,1'-Di(methoxymethylene)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, **1,1',3-Fc(CH$_2$OCH$_3$)$_2$(Bpin)**.
^{1}H NMR δ 1.12 (s, 12H), 3.10 (s, 3H), 3.16 (s, 3H), 4.09 (m, 4H), 4.16 (t, 2H, *J* = 1.3 Hz), 4.21 (s, 2H), 4.30 (d, 1H), 4.56 (d, 1H), 4.63 (s, 1H).

1,1'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene, 1,1'-Fc(Bpin)$_2$.
^{1}H NMR δ 1.12 (s, 12H), 4.37 (t, 4H, *J* = 1.7 Hz), 4.71 (t, 4H, *J* = 1.7 Hz).

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cymantrene, (C$_5$H$_4$Bpin)Mn(CO)$_3$.
^{1}H NMR δ 4.90 (t, 2H, *J* = 1.9 Hz), 4.09 (t, 2H, *J* = 1.9 Hz), 1.06 (s, 12H); ^{13}C NMR δ 24.6, 84.0, 85.3, 92.1.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2yl)cyclopentadienyl-molybdenum-tricarbonyl-methyl, ($C_5H_4Bpin)Mo(CO)_3(CH_3)$.
^{1}H NMR δ 5.22 (t, 2H, *J* = 2.6 Hz), 5.16 (t, 2H, *J* = 2.6 Hz), 1.19 (s, 12H), -0.01 (s, 3H); ^{13}C NMR δ 1.6, 4.6, 29.6, 83.4 (d, *J* = 27.4 Hz), 92.0 (d, *J* = 10.4 Hz), 93.3 (d, *J* = 10.5 Hz), 216.4.

General procedure for the Ir-catalyzed CH-activation
To a schlenk tube equipped with a reflux condenser, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 10.0 mg), dtbpy (0.03 mmol, 4.7 mg), and B_2pin_2 (1.0 mmol, 254.0 mg) were added. Octane (7 ml) and the respective ferrocene or half sandwich complex (2.0 mmol) were added, and the mixture was stirred at the given temperature for the given period of time. The reaction mixture was analyzed with GC and the pure product was isolated by column chromatography (silica gel, cyclehexane/ethyl acetate) whose purity was checked by GC and NMR.

Competition Experiment
A mixture of $[Ir(OMe)(cod)]_2$ (0.015 mmol, 10.0 mg), dtbpy (0.03 mmol, 4.7 mg), B_2pin_2 (1.0 mmol, 254.0 mg), $FcCOOCH_3$ (2.0 mmol, 488 mg) and 1,1´-$Fc(COOCH_3)_2$ (2.0 mmol, 604 mg) were stirred at 110º C for 17h. The products were separated and their yield was determined.

Suzuki Reaction
A mixture of FcBpin (0.25 mmol, 78 mg), 4-bromoacetophenone (0.3 mmol, 60 mg), $TBAF{\cdot}3H_2O$ (0.3 mmol, 95 mg), K_3PO_4 (0.3 mmol, 64 mg) $Ad_2PBn{\cdot}HBr$ (4 mol%, 5mg) and Na_2PdCl_4 (2 mol%, 1.5 mg) in toluene (3 ml) was heated to 80° C for 6 h. The mixture was cooled to room temperature, filtered and all volatiles were evaporated. Purification by column chromatography on silica (cyclohexane, ethyl acetate 5:1) yielded the product as orange crystals with spectroscopic data identical to those previously reported. [4]
Yield: 42 mg (55.2 %).

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